PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] :
B01D 53/94, 53/86, F01N 3/20

A1

(11) International Publication Number: WO 99/55446

(43) International Publication Date: 4 November 1999 (04.11.99)

(21) International Application Number: PCT/GB99/01205

(22) International Filing Date: 20 April 1999 (20.04.99)

(30) Priority Data:
9808876.8 28 April 1998 (28.04.98) GB

(71) Applicant (*for all designated States except US*): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): CHANDLER, Guy, Richard [GB/GB]; 30 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). RAJARAM, Raj, Raq [MU/GB]; 34 Buckland Avenue, Slough SL3 7PH (GB). GOERSMANN, Claus, Friedrich [DE/GB]; 39 Cromwell Road, Cambridge CB1 3EB (GB). SELF, Valerie, Anne [GB/GB]; 34 Frank Lunnon Close, Bourne End, Buckinghamshire SL8 5UP (GB).

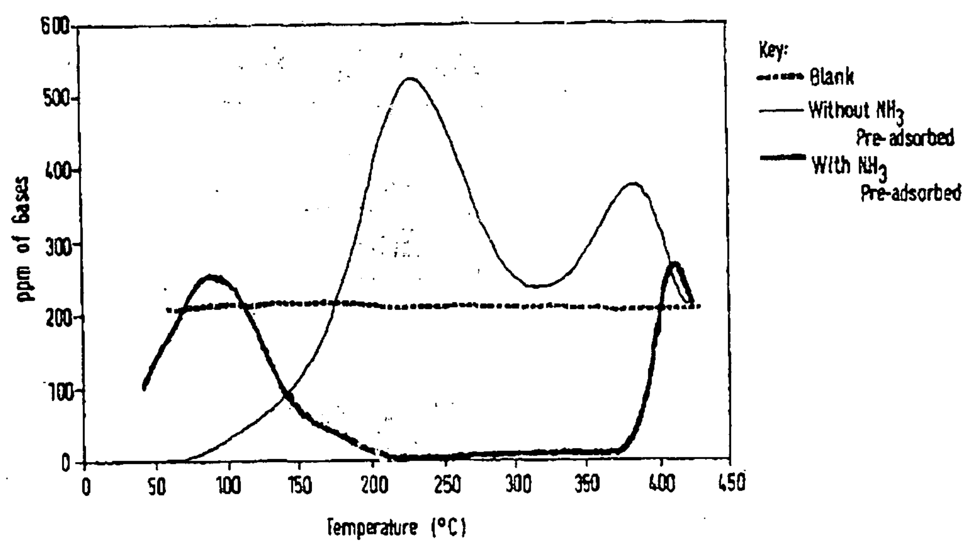
(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS AND APPARATUS FOR REDUCING THE NITROGEN OXIDE CONTENT IN EXHAUST GASES BY THE CONTROLLED ADDITION OF NH3

Effect of Adsorbed NH_3 on NO_x Activity of Cu/ZSM5
200 ppm NO, 12% O_2, 4% CO_2, 200 ppm CO



(57) Abstract

In the reduction of quantities of No_x in the exhaust gases of lean burn engines such as diesel engines, using a selective reduction catalyst and a source of ammonia, the present invention improves overall conversion by supplying ammonia or a precursor intermittently so that it is adsorbed and desorbed during the engine operating cycle.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PROCESS AND APPARATUS FOR REDUCING THE NITROGEN OXIDE CONTENT IN EXHAUST GASES BY THE CONTROLLED ADDITION OF NH3

This invention concerns combatting air pollution from the exhaust gas of a lean burn engine. In particular, it concerns apparatus for, and a method of, reducing the content of nitrogen oxides (NOx) in such gas.

Lean burn engines (which have an air-fuel ratio greater than 14.7, generally in the range 19-50) exhibit higher fuel economy and lower hydrocarbon emissions than do stoichiometrically operated engines and are increasing in number. Emissions from diesel engines are now being regulated by legislation, and whilst it is not too difficult to meet regulations on hydrocarbon or CO emissions, it is difficult to meet regulations on NOx emissions. Since exhaust gas from lean burn engines such as diesel engines is high in oxygen content throughout the engine cycle, it is more difficult to reduce NOx to nitrogen than in the case of stoichiometrically operated engines. The difficulty is compounded by the lower gas temperature. Various approaches are being considered to reduce NOx under the oxidising conditions. One approach is that of selective catalytic reduction (SCR) with hydrocarbon, but a catalyst of sufficient activity and durability to achieve the required conversion has not been found. Another approach is to adsorb the NOx by an adsorbent when the exhaust gas is lean (*ie* when there is a stoichiometric excess of oxygen) and release and reduce the adsorbed NOx when the exhaust gas is rich, the exhaust gas being made rich periodically. During the lean operation, NO is oxidised to NO_2 which can then react readily with the adsorbent surface to form nitrate. This approach, though, is constrained at low temperature by restricted ability to form NO_2 and by adsorbent regeneration and at high temperature by sulphur poisoning. Most adsorbents operate in a certain temperature window and are deactivated by sulphate formation. The approach of the present invention is that of SCR of NOx by NH_3. This approach has been applied to static diesel engines using a V_2O_5-TiO_2 type catalyst.

The application of NH_3 SCR technology to the control of NOx emission from lean burn vehicles, however, requires a suitable NH_3 supply strategy, especially at low temperature, for various reasons. The engine-out NOx varies with temperature, so the amount of NH_3 supplied must be well controlled as a function of the temperature to maintain

the appropriate stoichiometry for the reaction; an insufficient supply of NH_3 results in inadequate NOx reduction, whilst an excess may cause NH_3 to slip past the catalyst. Whilst at sufficiently high temperature, the catalyst can selectively oxidise that excess NH_3 to N_2, at low temperature, the unreacted NH_3 will be emitted as such. Even if the proper stoichiometry of NH_3 is provided, the catalyst may not be sufficiently active at low temperature to react all the NH_3 with the NOx. For example, Figure 1 shows the reaction of NH_3 with NOx over a non-metallised zeolite as a function of temperature at a stoichiometry of 1:1 at an inlet concentration of 200ppm. It can be seen that at temperatures below 300°C the reduction does not proceed to any significant extent. Furthermore, it has been reported that the presence of excess NH_3 at low temperature could lead to the formation of NH_4NO_3 and $(NH_4)_2SO_4$. There is also evidence that the presence of excess gas phase NH_3 can inhibit the NH_3 SCR reaction over some catalysts at low temperature. Urea is usually the preferred form of storing NH_3 on a vehicle. Urea is readily available and is stable in water solution. However, it only hydrolyses readily to NH_3 at temperatures greater than 150°C, and may not be a suitable source of NH_3 at low temperature. Exhaust gas temperatures, though, vary over an engine cycle and for the average light duty diesel car a significant fraction of that cycle is at low temperature. Thus, the control of NOx at low temperature is a problem.

The present invention provides an improved apparatus and method for reducing the content of NOx.

Accordingly, the invention provides apparatus for reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which apparatus comprises:

(a) exhaust apparatus through which the exhaust gas flows;

(b) selective catalytic reduction catalyst in the exhaust apparatus, the catalyst catalysing the reduction of the NOx by ammonia to nitrogen and adsorbing and desorbing ammonia during the engine cycle;

(c) a source of the ammonia;

(d) supply means to supply the ammonia from the source to the catalyst; and

(e) means to make the supply of ammonia intermittent during the engine cycle;

whereby the catalyst adsorbs ammonia during its supply and the ammonia which has been adsorbed reacts with the NOx when the ammonia is not supplied.

The invention provides also a method of reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which method comprises passing the exhaust gas over a selective catalytic reduction catalyst which catalyses the reduction of the NOx by ammonia to nitrogen and which adsorbs and desorbs ammonia during the engine cycle, ammonia being supplied intermittently to the catalyst during the engine cycle, the catalyst adsorbing ammonia during its supply and the ammonia which has been adsorbed reacting with the NOx when the ammonia is not supplied.

We have discovered that ammonia can be adsorbed on a SCR catalyst and thereafter used in the NOx reduction when ammonia is not being supplied. It is an advantage to be able to achieve the NOx reduction while supplying the ammonia intermittently. In particular, the ammonia supply can be halted and yet NOx reduction occur when the temperature of the catalyst is low and supply would have the problems referred to above. The stored ammonia can be used as reductant for NOx over the same catalyst without the presence of gas phase NH_3.

The ammonia can be supplied without the exhaust gas so that the catalyst adsorbs the ammonia and then the exhaust gas passed over the catalyst for the NOx reduction to occur Preferably, however, the exhaust gas is passed continuously over the catalyst.

The invention uses adsorption and desorption characteristics of the required catalyst. A higher amount of NH_3 will be adsorbed, and hence be available for subsequent reaction, if adsorption is at a lower temperature than temperatures at which the catalyst adsorbs less NH_3. Preferably NH_3 is adsorbed at a temperature at which a large amount is adsorbed; the temperature is preferably below that of maximum desorption. The temperature, however, is preferably above that at which any significant formation of ammonium salts occurs. Figure 2 shows the desorption profile from zeolite ZSM5 (non-metallised) of NH_3 which had been pre-adsorbed at 100°C. It can be seen that at say 300°C more NH_3 is retained,

adsorbed, than at say 400°C, and that the temperature of maximum desorption is about 370°C. Bearing in mind that the desorption of NH_3 is endothermic, it can also be seen that if NH_3 were adsorbed at say 300°C and then heated, NH_3 would be desorbed in accordance with the graph so that less would be available for subsequent reaction, while if NH_3 were adsorbed at the same temperature, 300°C, and cooled, NH_3 would not be desorbed so the adsorbed NH_3 would be available for subsequent reaction. NH_3 stored on the ZSM5 catalyst at 250°C can effectively be used to reduce NOx at a temperature as low as 150°C under exhaust conditions simulating those of a light duty diesel car. Figure 3 shows the NH_3 uptake of ZSM5 catalyst (non-metallised) from a gas mixture containing 4.5% CO_2, 12% O_2, 4.5% H_2O, 200ppm CO, 100ppm C_3H_6, 20ppm SO_2 and 200ppm NH_3 with the balance N_2 at 250°C, and Figure 4 shows the subsequent reaction of that adsorbed NH_3 with NOx at 150°C. It can be seen that significant amounts of NOx are reduced by the adsorbed NH_3 over a period of time and that as the stored NH_3 is being consumed, the reduction reaction declines with time. When the temperature rises in the engine cycle, however, NH_3 can be supplied again, and hence adsorbed NH_3 replenished. Accordingly, the problem of supplying NH_3 at low temperature can be overcome by halting its supply and using adsorbed NH_3. The amount of NH_3 adsorbed on a fixed weight of catalyst can be increased by increasing its partial pressure in the gas mixture. For example, Table 1 gives the amount of NH_3 adsorbed by a zeolite at 250°C from a simulated gas mixture of differing NH_3 concentrations.

TABLE 1

NH_3 Adsorption as a Function of NH_3 Concentration

NH_3 Concentration (ppm)	Amount NH_3 Adsorbed (mmoles per g)
200	0.63
500	1.22
1000	1.48

The means to make the supply of ammonia intermittent during the engine cycle in the present apparatus can be a switch which switches the ammonia supply on and off dependent on the level of NOx conversion occurring over the SCR catalyst. Preferably, however, the means to make the supply of ammonia intermittent comprises a switch to switch on the means to supply the ammonia when the temperature of the catalyst rises above a set level (i) during the engine cycle, and to switch off the means to supply the ammonia when the temperature of the catalyst falls below a set level (ii). The set level (i) is preferably in the range 250-400°C, especially in the range 250-350°C. The set level (ii) is preferably in the range 200-250°C.

The ammonia can be supplied for instance 1-30 times per minute.

The source of ammonia and means to supply it from the source to the catalyst can be conventional. Compounds of ammonia as a solid or a solution in water are preferred. The compounds are preferably urea or ammonium carbamate. The means to supply the ammonia from the source to the catalyst can be a pipe through which it is injected into the exhaust gas up-stream of the catalyst. Thus, the present invention can be employed to provide a method of promoting the conversion of NOx under oxidising conditions in an exhaust fitted with a means of injecting NH_3 and a catalyst which adsorbs NH_3 during parts of the engine cycle in which the exhaust gas is sufficiently warmed for the hydrolysis of NH_3 precursor and injection of ammonia and ammonia is adsorbed by the catalyst for use as reductant for NOx during parts of the engine cycle in which the exhaust gas is cooler, without the need for the continuous injection of NH_3 into the exhaust gas.

It can be seen that the invention provides an exhaust system for an engine operating generally under lean conditions, which exhibits a higher exhaust gas temperature and a lower exhaust gas temperature, the lower exhaust gas temperature being inadequate for the effective hydrolysis of NH_3 precursor and injection of NH_3 (generally a temperature below 200°C), and an NH_3 SCR catalyst arranged and constructed so that during the higher exhaust gas temperature parts of the engine cycle the catalyst adsorbs NH_3 and during the lower

exhaust gas temperature parts of the engine cycle the adsorbed NH_3 is used as reductant for NOx.

The catalyst can be any which has the required characteristics of the present catalyst. The same material can both selectively catalyse the reduction and also adsorb and desorb the ammonia, and this is preferred. However, different materials in the catalyst can perform the two functions, one material catalysing and one material adsorbing and desorbing. When different materials are employed, they can be physically separate or, preferably, in admixture one with another. A zeolite can perform both functions or a zeolite can be employed which performs one function together with a different material, which may or may not be a zeolite, which performs the other function. The catalyst preferably comprises a zeolite. The zeolite can be metallised or non-metallised, and can have various silica-to-alumina ratios. Examples are metallised or non-metallised ZSM5, mordenite, γ zeolite and β zeolite. Preferred is ZSM5 or ion-exchanged or metal impregnated ZSM5 such as Cu/ZSM5. It may be desirable that the zeolite contains metal, especially Cu, Ce, Fe or Pt; this can improve the low temperature SCR activity. The zeolite can contain for instance 1-10% of metal by weight. The catalyst should have an appropriate structure, for instance in terms of pore size or surface acid sites, to trap and release NH_3.

The catalyst is preferably carried out on a support substrate, in particular a honeycomb monolith of the flow-through type. The monolith can be metal or ceramic. The substrate can be conventional.

Nitrogen oxide (NO) is usually the most abundant nitrogen oxide in an engine exhaust stream, but at lower temperatures the reaction of the adsorbed NH_3 on a zeolite catalyst occurs more readily with NO_2 than with NO. Accordingly it is often desirably to oxidise NO to NO_2 up-stream of the SCR catalyst, particularly at low temperature.

The present engine can be a diesel or petrol (gasoline) engine. The diesel engine can be a light duty or heavy duty diesel engine. The engine is preferably that of a vehicle.

The invention is illustrated by the accompanying drawings, which are graphs in which:

Figure 1 shows NOx and NH_3 concentrations in simulated exhaust gas against temperature after treatment by zeolite ZSM5, the NH_3 being supplied continuously;

Figure 2 shows the temperature programmed desorption (TPD) of NH_3 from ZSM5 which had been pre-adsorbed at 100°C, the graph showing, in arbitrary units, the concentration of ammonia in the gas against temperature;

Figure 3 shows the NH_3 concentration in a full simulated exhaust gas mixture containing 4.5% CO_2, 12% O_2, 4.5% H_2O, 200ppm CO, 100ppm C_3H_6, 20ppm SO_2 and 200ppm NH_3 with the balance N_2 after passage over ZSM5 at 250°C against time, and hence shows the NH_3 uptake by the zeolite;

Figure 4 shows the NOx concentration remaining in simulated exhaust gas after passage over the zeolite containing adsorbed NH_3 resulting from the adsorption shown in Figure 3 against time;

Figure 5 shows the NOx concentration remaining in simulated exhaust gas containing 200ppm NO, 200ppm CO, 12% O_2 and 14% CO_2 with the balance N_2 after passage over ZSM5 with and without pre-adsorption of NH_3 against temperature;

Figure 6 shows the corresponding effect to that shown in Figure 5 of successive cycles of the NH_3 pre-adsorption followed by subjection to the simulated exhaust gas;

Figure 7 corresponds to Figure 5 but with the simulated exhaust gas containing also hydrocarbon;

Figure 8 corresponds to Figure 7 but with the simulated exhaust gas containing also H_2O and SO_2;

Figure 9 corresponds to Figure 5 but with the simulated exhaust gas containing NO_2 instead of NO;

Figure 10 corresponds to Figure 9 but with the simulated exhaust gas containing also hydrocarbon;

Figure 11 corresponds to Figure 10 but with the simulated exhaust gas containing also H_2O and SO_2;

Figure 12 shows NOx concentration and temperature against time during part of an engine cycle;

Figure 13 corresponds to Figure 12 but shows the effect of intermittent supply of NH_3;

Figure 14 shows the NOx concentration remaining in simulated exhaust gas after passage over Cu/ZSM5 with and without pre-adsorption of NH_3 against temperature; and

Figure 15 shows the NOx concentration remaining in simulated exhaust gas which is that used in relation to Figure 14 but containing also hydrocarbon, H_2O and SO_2, after passage over Cu/ZSM5 with pre-adsorption of NH_3 against temperature.

Figures 1-4 are discussed further hereinbefore, and Figures 5-15 hereinafter.

The invention is illustrated also by the following Examples.

EXAMPLE 1

Reaction of NO With Pre-adsorbed NH_3 Over Non-metallised ZSM5

This Example shows the effect of pre-adsorbing NH_3 at 250°C on the conversion of NOx over a non-metallised zeolite in a simple gas mixture containing NOx, CO, CO_2 and O_2 during a light-off test from room temperature to 400°C. The gas stream containing NO (200ppm), CO (200ppm), O_2 (12%), CO_2 (14%) with the balance N_2 at a flow rate of 2 litres per minute was first passed over the non-metallised zeolite (0.4g) from room temperature to 400°C at a heating rate of 50°C per minute and the NOx at the outlet measured. In a subsequent experiment, the catalyst temperature was first raised to 250°C and 200ppm NH_3 was added to the gas stream, the zeolite was exposed to that stream for 5 minutes and then the NH_3 switched off, and the catalyst was cooled to room temperature and the rapid light-off repeated. Figure 5 shows the outlet NOx concentration for these experiments. It can be seen that in the case where NH_3 was not pre-adsorbed over the catalyst, some of the NOx is adsorbed on the zeolite at low temperature and is then subsequently released between 150°C and 350°C, but that when NH_3 was pre-adsorbed on the zeolite, the zeolite did not adsorb a significant amount of NOx at low temperature. Furthermore, it can be seen that a decrease in the outlet NOx concentration occurs from 150°C to 450°C due to the reaction of the NOx with the pre-adsorbed NH_3. This effect of reacting the adsorbed NH_3 with the

NOx can be repeated over successive cycles with NH_3 injection at 250°C between each cycle, as is shown in Figure 6.

We have also shown that even in the presence of other gaseous components such as hydrocarbon, H_2O and SO_2, the adsorption of NH_3 will readily occur on the zeolite and can be used to reduce NOx. For example, Figure 7 shows the effect of adding 200ppm C_3H_6 to the gas mixture in similar tests to those described above and Figure 8 shows the effect of further addition of H_2O (10%) and SO_2 (20ppm). It can be seen that in both cases NOx was reduced by the adsorbed NH_3.

EXAMPLE 2

Reaction of NO_2 with Pre-adsorbed NH_3 Over Non-metallised ZSM5

The selective catalytic reduction of NOx by NH_3 under oxidising conditions proceeds more rapidly at low temperature if NO_2 instead of NO is present. The present Example shows that NH_3 pre-adsorbed on a zeolite catalyst can be used to reduce NO_2 even at a temperature as low as 100°C. This was demonstrated by rapid light-off tests analogous to that described above in Example 1. In the first experiment, a simple gas mixture containing NO_2 (200ppm), CO (200ppm), O_2 (12%), CO_2 (14%) with the balance N_2 at a flow rate of 2 litres per minute was passed over the non-metallised zeolite (0.4g) from room temperature to 400°C at a heating rate of 50°C per minute. In a subsequent experiment, the catalyst temperature was first raised to 250°C and 200ppm NH_3 was added to the gas stream, the zeolite was exposed to that stream for 5 minutes and then the NH_3 was switched off, and the catalyst was cooled to room temperature and the rapid light-off repeated. Figure 9 shows the outlet NOx concentration from these experiments. It can be seen that in the absence of pre-adsorbed NH_3, NO_2 is adsorbed at low temperature over the zeolite and is released between 100°C and 300°C, but when NH_3 was pre-adsorbed on the catalyst, significant NOx reduction is shown over the entire temperature window up to 400°C.

We have also shown that even in the presence of hydrocarbon, H_2O and SO_2 adsorbed NH_3 will readily react with NO_2. Figure 10 shows the effect of adding C_3H_6 on the reaction

of pre-adsorbed NH_3 with NOx, and Figure 11 demonstrates the effect with addition of H_2O and SO_2.

EXAMPLE 3

Reaction of NO_2 With Pre-adsorbed NH_3 Over Non-metallised ZSM5 in Cycle Test

In most cases, exhaust gas temperature varies during an engine cycle and for a significant fraction of that time the temperature can be low. We have shown that by injecting NH_3 over a set temperature during the cycle, the adsorbed NH_3 can subsequently be utilised in reducing NOx at both low and high temperature. In the experiment, exhaust gas containing CO_2 (14%), O_2 (12%), H_2O (10%), CO (200ppm), C_3H_6 (200ppm), SO_2 (20ppm) and NO_2 (200ppm) was cycled between 150°C and 350°C with a dwell of approximately 5 minutes at 250°C during the cooling-down part of the cycle. The NH_3 injection was switched on when the temperature was at 350°C and switched off when the temperature fell to 250°C. Figure 12 shows the outlet NOx concentration and the temperature against time without any NH_3 injection, and Figure 13 shows the effect of the cycling with the intermittent injection of NH_3. In both Figures, the ordinate scale gives the degrees C for the temperature graph and the parts per million (ppm) for the NOx graph.

EXAMPLE 4

Reaction of NO With Pre-adsorbed NH_3 Over Cu/ZSM5

This Example shows the effect of pre-adsorbing NH_3 at 250°C on the conversion of NOx over a Cu-impregnated ZSM5 (containing 5% copper by weight) in a simple gas mixture containing NOx, CO, CO_2 and O_2 during a light-off test from room temperature to 400°C. The gas stream containing NO (200ppm), CO (200ppm), O_2 (12%), CO_2 (14%) with the balance N_2 at a flow rate of 2 litres per minute was first passed over the Cu/ZSM5 (0.4g) from room temperature to 400°C at a heating rate of 50°C per minute and the NOx at the outlet measured. In a subsequent experiment, the catalyst temperature was first raised to 250°C and 200ppm NH_3 was added to the gas stream, the Cu/ZSM5 was exposed to that stream for 5 minutes and then the NH_3 was switched off, the catalyst was cooled to room

temperature rapidly and the light-off repeated. Figure 14 shows the outlet NOx concentration for these experiments. It can be seen that in the case where NH_3 was not pre-adsorbed on the catalyst, some of the NOx is adsorbed on the zeolite at low temperature, and is then subsequently released at higher temperature, but the pre-adsorption of NH_3 at 250°C suppresses the amount of NOx adsorbed at low temperature, with significant NOx reduction by the pre-adsorbed NH_3 at temperatures greater than 125°C.

Similarly, even in the presence of other gaseous components such as hydrocarbon, H_2O and SO_2 the adsorption of NH_3 will occur readily over the Cu/ZSM5 and can be used to reduce NOx. For example, Figure 15 shows the effect of pre-adsorbing NH_3 on the Cu/ZSM5 at 250°C from a gas mixture containing NO, H_2O, CO_2, CO, C_3H_6, SO_2 and O_2 and the reduction of NOx by the adsorbed NH_3 during a light-off test.

CLAIMS

1. Apparatus for reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which apparatus comprises:

(a) exhaust apparatus through which the exhaust gas flows;

(b) selective catalytic reduction catalyst in the exhaust apparatus, the catalyst catalysing the reduction of the NOx by ammonia to nitrogen and adsorbing and desorbing ammonia during the engine cycle:

(c) a source of the ammonia;

(d) supply means to supply the ammonia from the source to the catalyst; and

(e) means to make the supply of ammonia intermittent during the engine cycle:

whereby the catalyst adsorbs ammonia during its supply and the ammonia which has been adsorbed reacts with the NOx when the ammonia is not supplied.

2. Apparatus according to claim 1 adapted to pass the exhaust gas continuously over the catalyst.

3. Apparatus according to claim 1 or 2 wherein the means to make the supply of ammonia intermittent during the engine cycle, (e), comprises a switch to switch on the supply means, (d), when the temperature of the catalyst rises above a set level, (i), during the engine cycle, and to switch off the supply means, (d), when the temperature of the catalyst falls below a set level, (ii).

4. Apparatus according to claim 3 wherein the set level (i) is in the range 250-400°C and the set level (ii) is in the range 200-250°C.

5. Apparatus according to any one of claims 1-4 wherein the catalyst comprises the same material which both selectively catalyses the reduction and also adsorbs and desorbs the ammonia.

6. Apparatus according to any one of the preceding claims wherein the catalyst comprises a zeolite.

7. Apparatus according to claim 6 wherein the zeolite is non-metallised.

8. Apparatus according to claim 7 wherein the zeolite is ZSM5.

9. Apparatus according to claim 6 wherein the zeolite contains metal.

10. Apparatus according to claim 9 wherein the zeolite is Cu/ZSM5.

11. A method of reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which method comprises passing the exhaust gas over a selective catalytic reduction catalyst which catalyses the reduction of the NOx by ammonia to nitrogen and which adsorbs and desorbs ammonia during the engine cycle, ammonia being supplied intermittently to the catalyst during the engine cycle, the catalyst adsorbing ammonia during its supply and the ammonia which has been adsorbed reacting with the NOx when the ammonia is not supplied.

Fig. 1. NO_x and NH_3 conversion on ZSM5 in dynamic conditions 0·4g ZEOLITE 2 Litres per minute and 200ppm NO_x

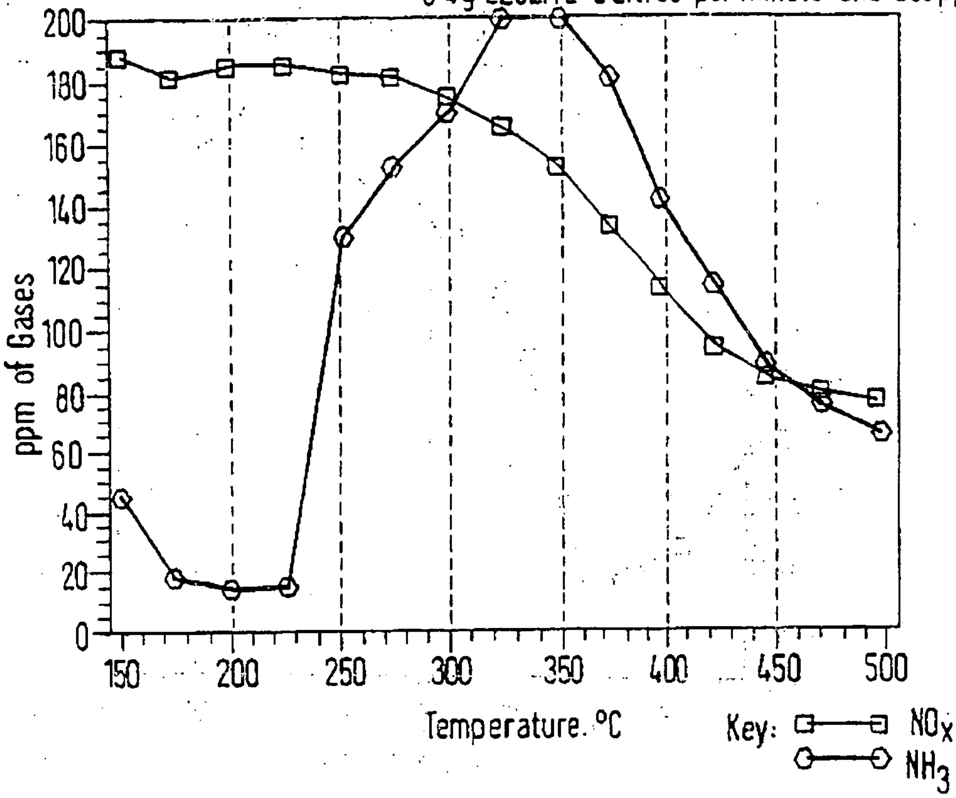


Fig. 2. TPD of NH_3 from ZSM5

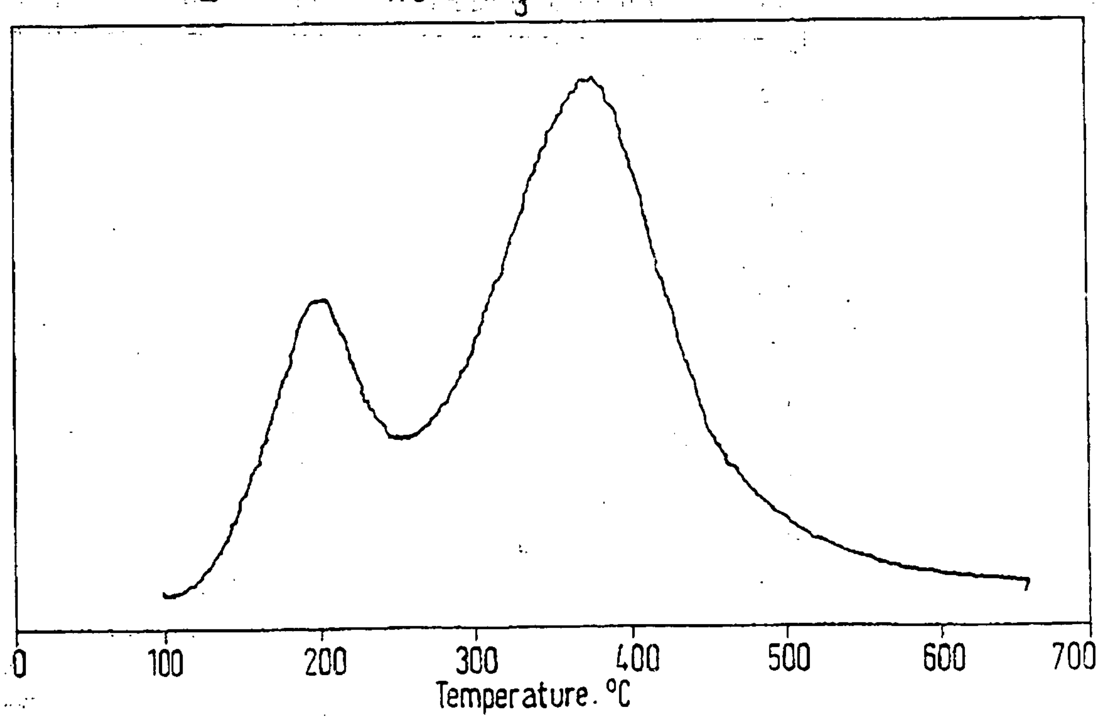


Fig.3. Adsorption of NH_3 on ZSM5 at 250°C in Full gas Mixture 0·4g ZEOLITE 2 Litres per minute and 200 ppm NO_x

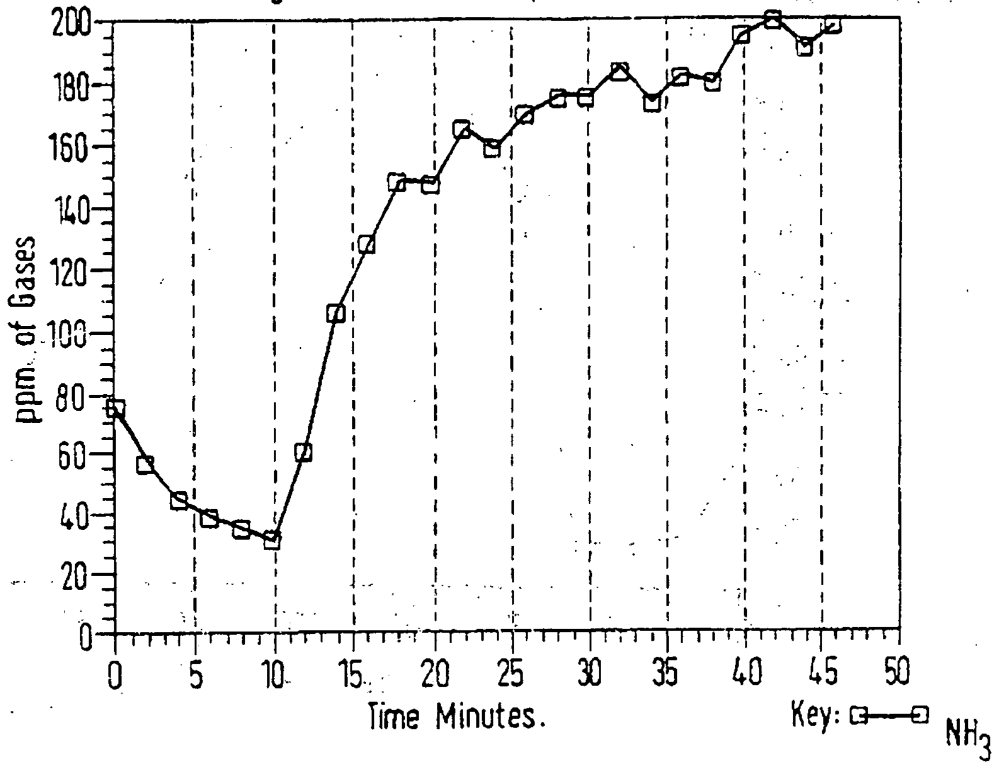


Fig.4. Reaction of adsorbed NH_3 with NO_2 on ZSM5 at 150°C in Full gas Mixture 0·4g ZEOLITE 2 Litres per minute and 200 ppm NO_x

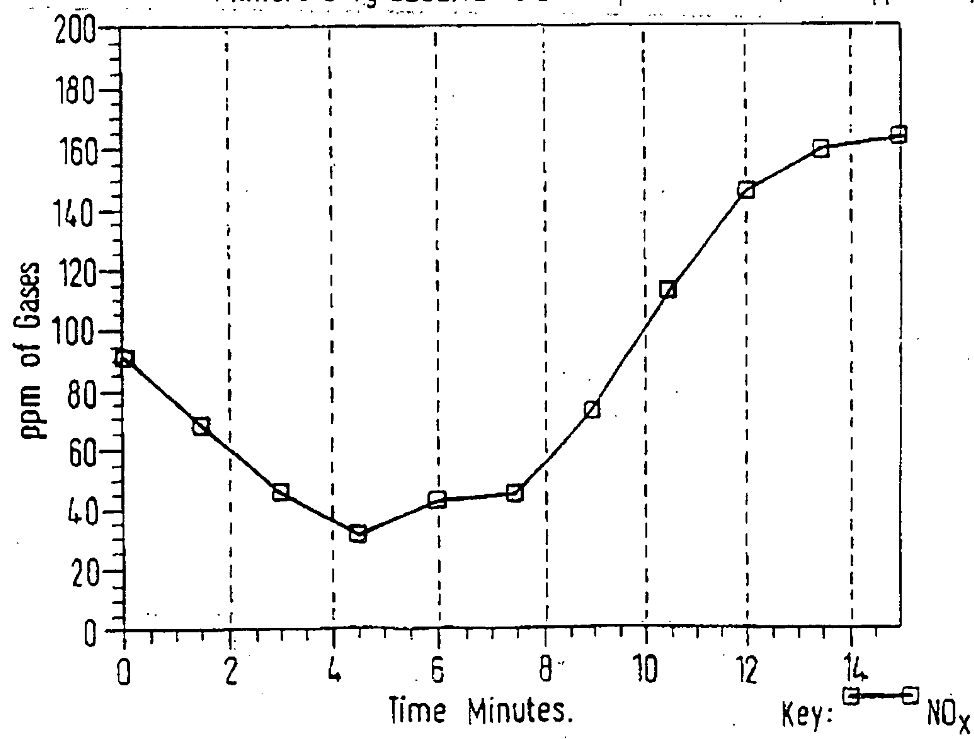


Fig.5. Effect of Pre-Adsorbed NH_3 on NO_x Activity of ZSM5
200ppm NO, 12% O_2, 14% CO_2, 200ppm CO.

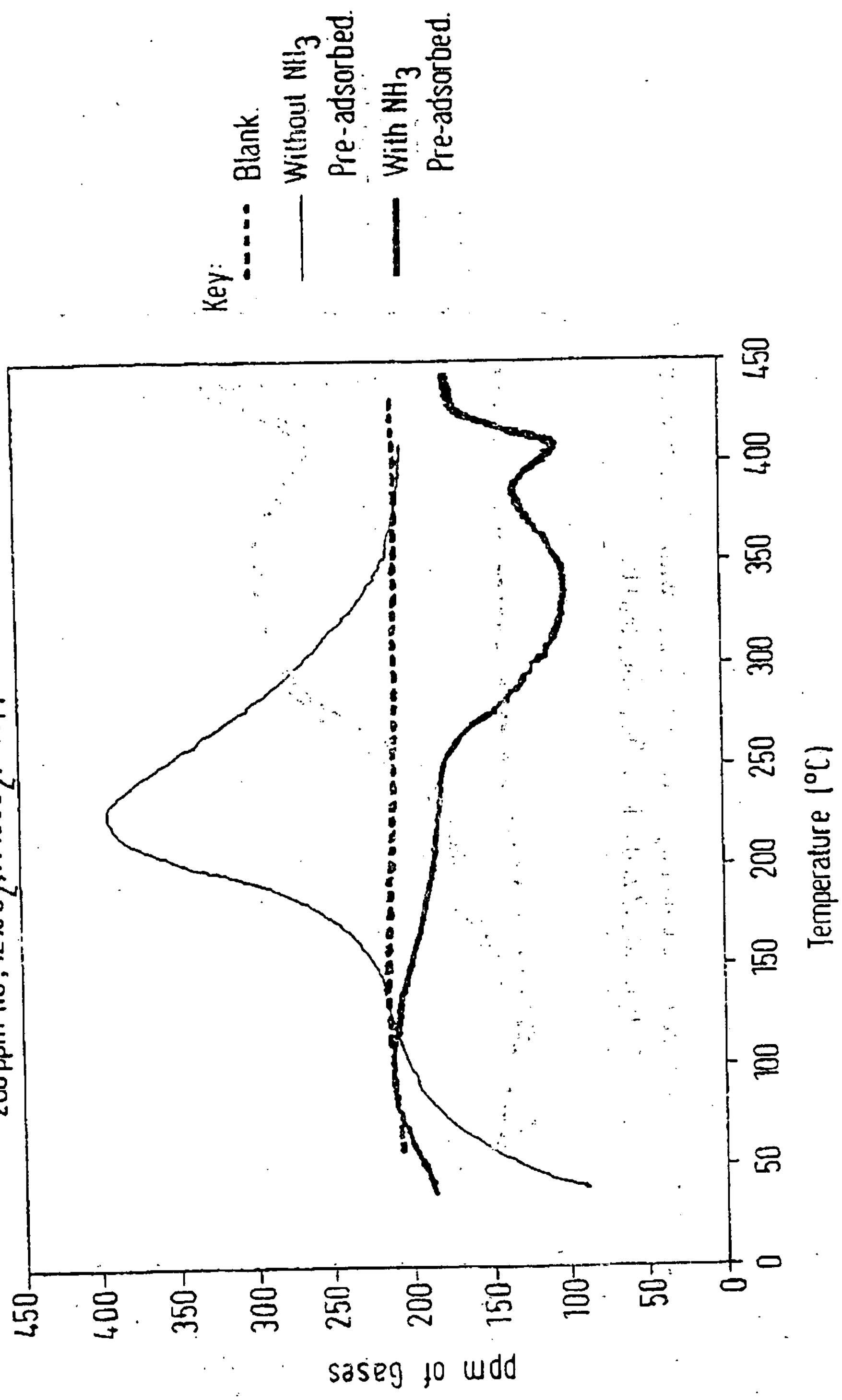


Fig.6. Effect of repeated cycle on NO_x Activity of ZSM5 with pre-adsorbed NH_3
200 ppm NO, 12% O_2, 14% CO_2, 200 ppm CO.

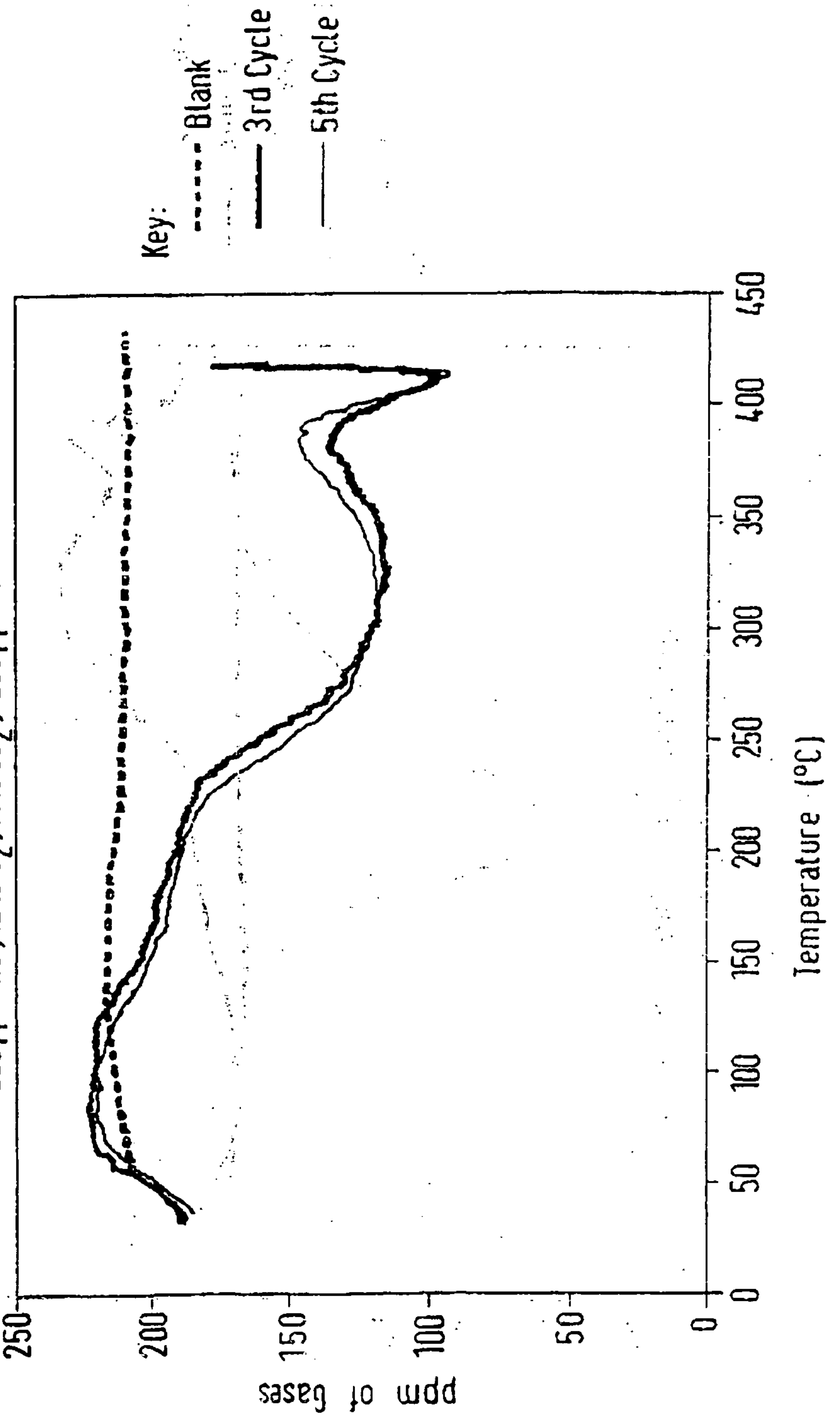


Fig.7. Effect of Adsorbed NH_3 on NO_x Activity of ZSM5 in presence of Hydrocarbon
200 ppm NO, 12% O_2, 14% CO_2, 200ppm CO, 200ppm C_3H_6

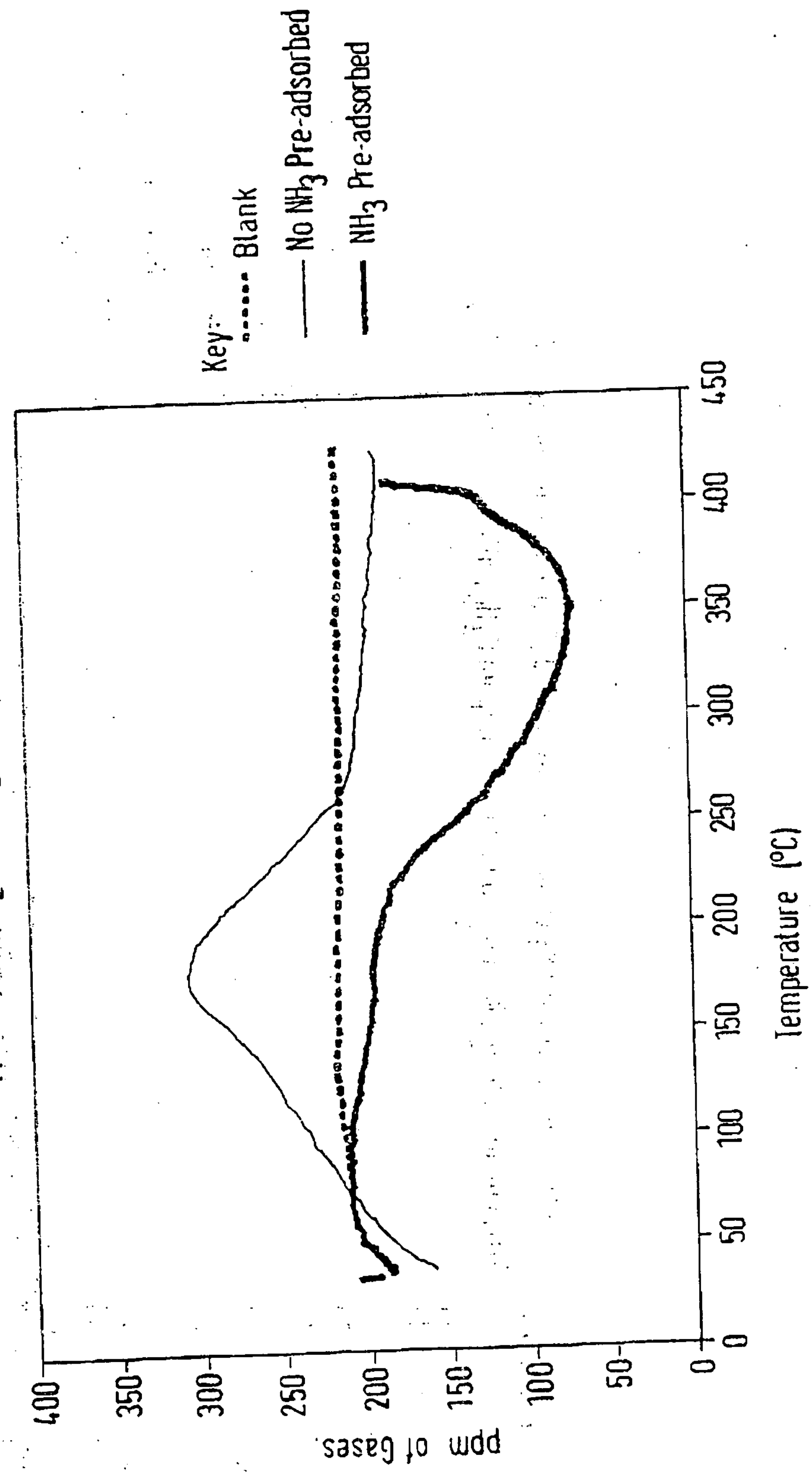


Fig.8.

Effect of Adsorbed NH_3 on NO_x Activity of ZSM5 in Full gas mixture

200 ppm NO, 12% O_2, 14% CO_2, 200 ppm CO, 200 ppm C_3H_6, 10% H_2O, 20 ppm SO_2

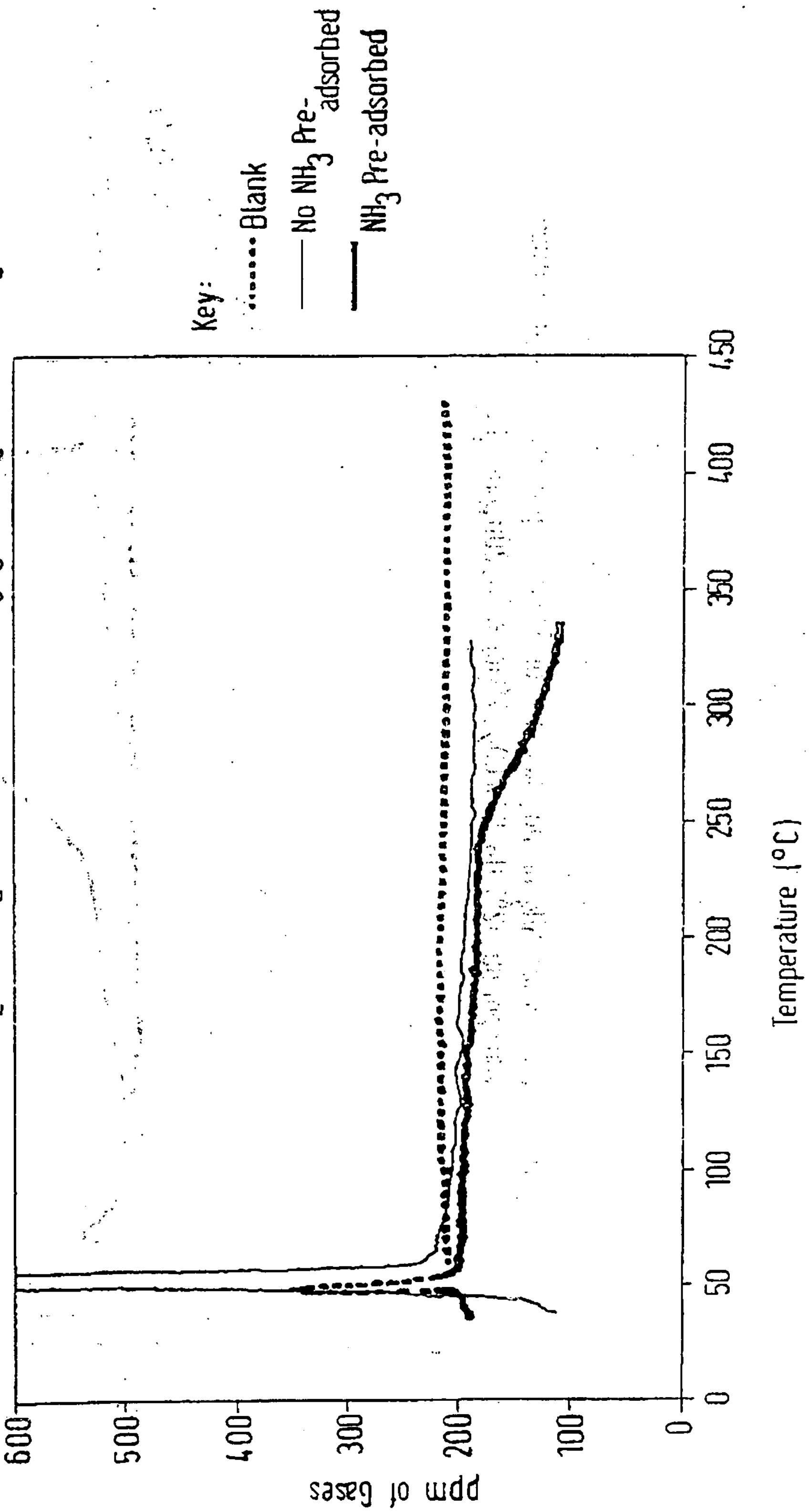


Fig.9.

Effect of Adsorbed NH_3 on NO_2 Activity of ZSM5
200ppm NO_2, 12% O_2, 14% CO_2, 200ppm CO

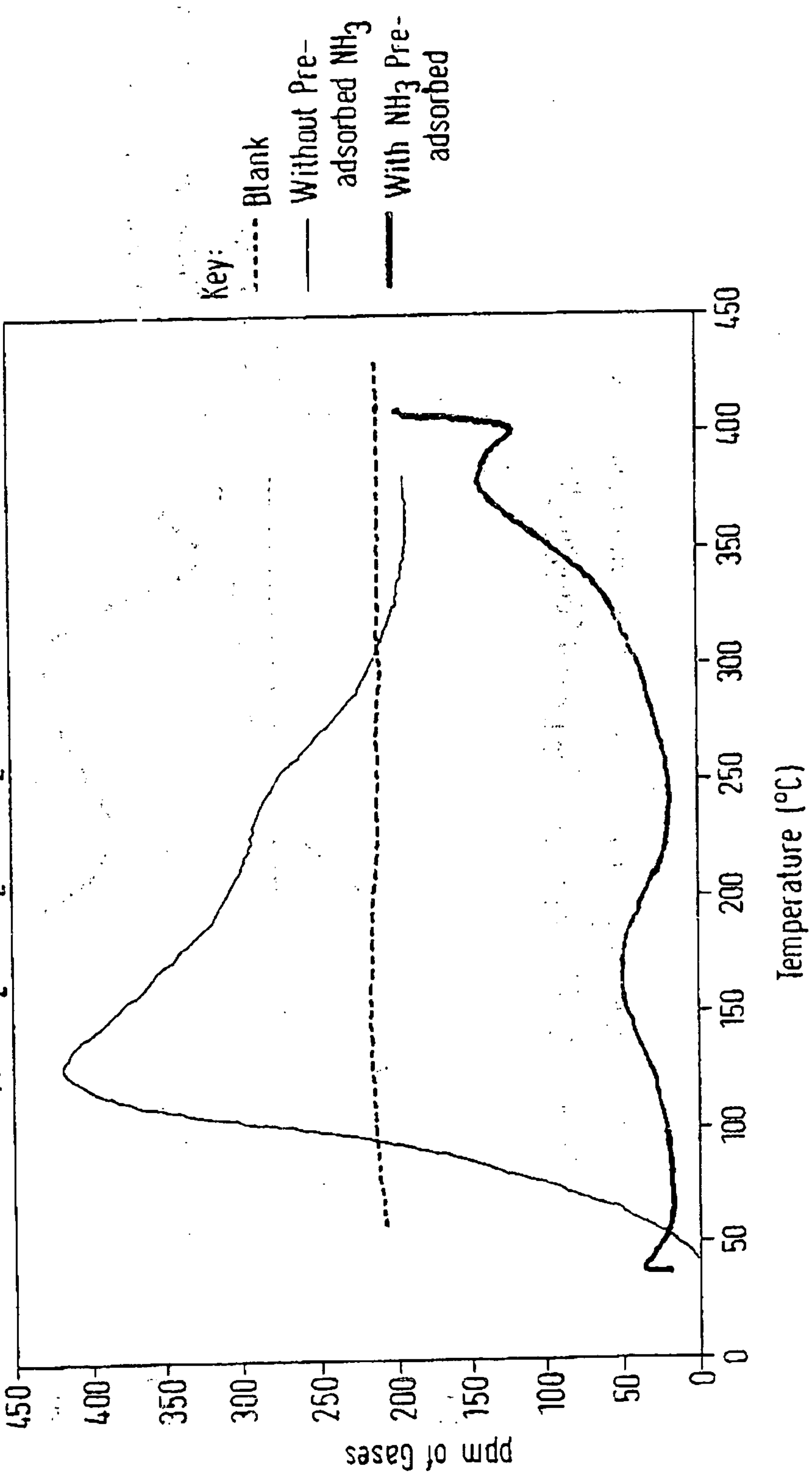


Fig.10. Effect of Adsorbed NH_3 on NO_2 Activity of ZSM5 with Hydrocarbon
200ppm NO_2, 12% O_2, 14% CO_2, 200ppm CO, 200ppm C_3H_6

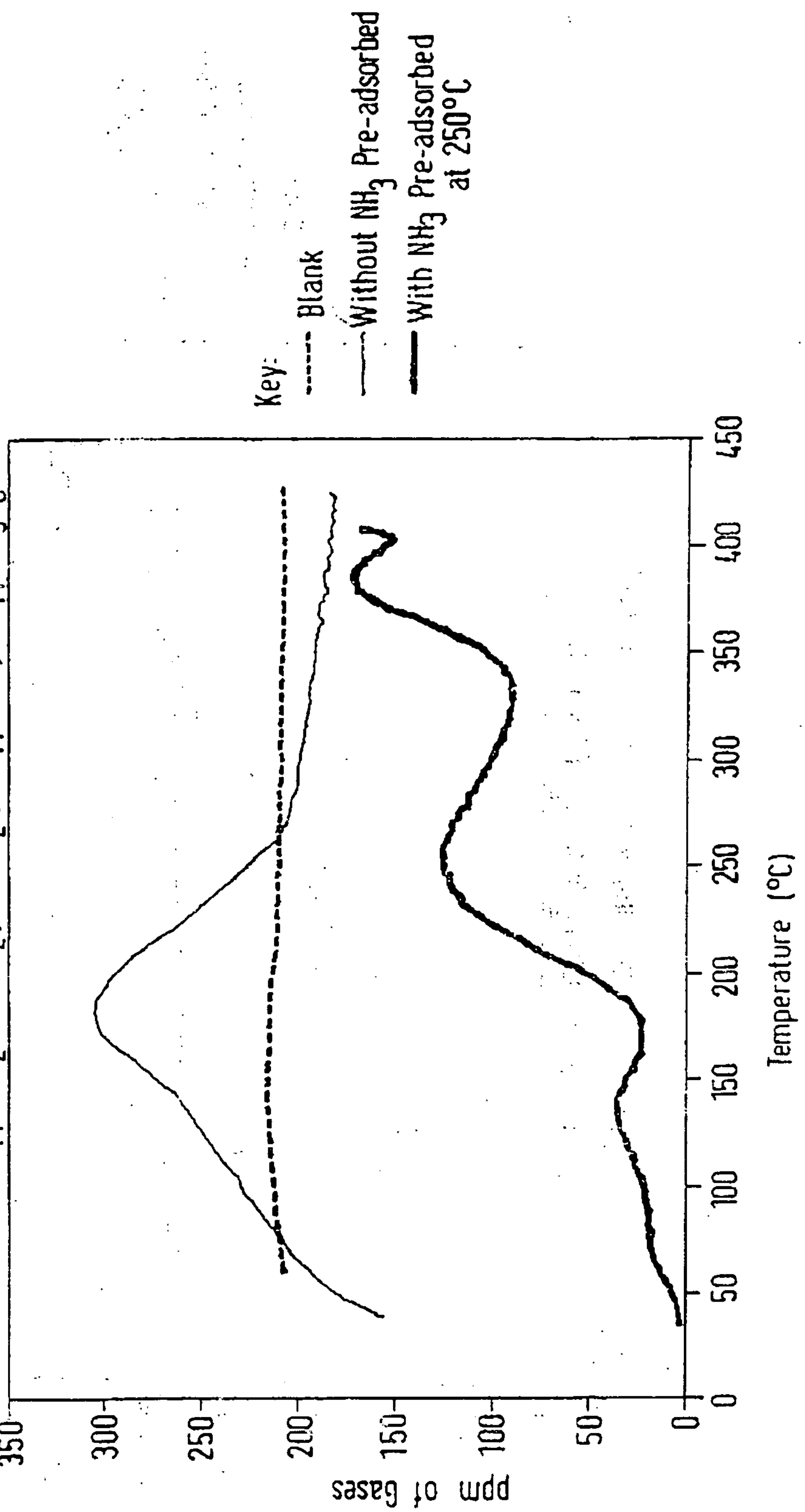


Fig.11. Effect of Adsorbed NH_3 on NO_2 Activity of ZSM5 in Full gas mixture
200ppm NO_2, 12% O_2, 14% CO_2, 200ppm CO, 200ppm C_3H_6, 10% H_2O, 20ppm SO_2

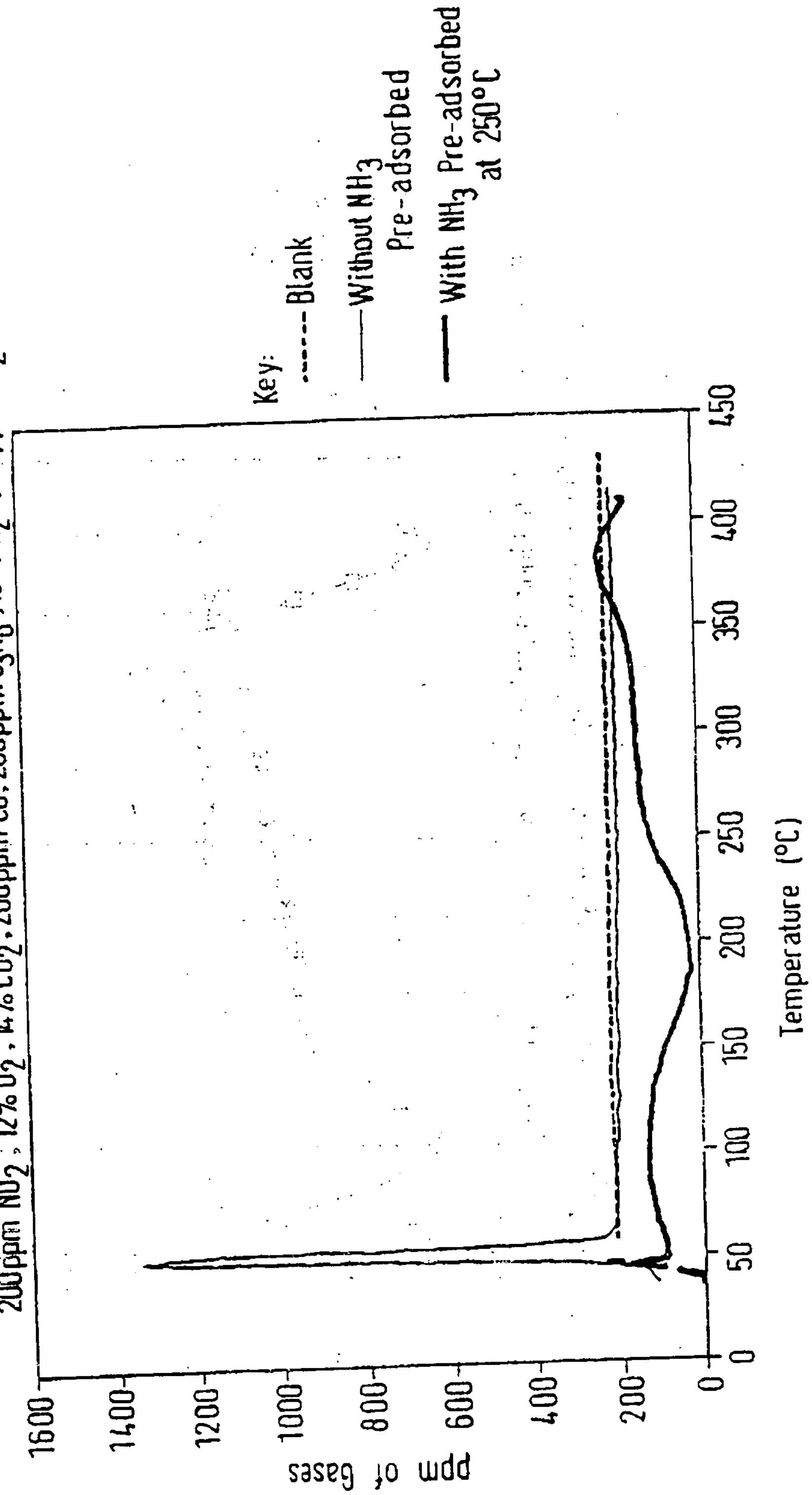
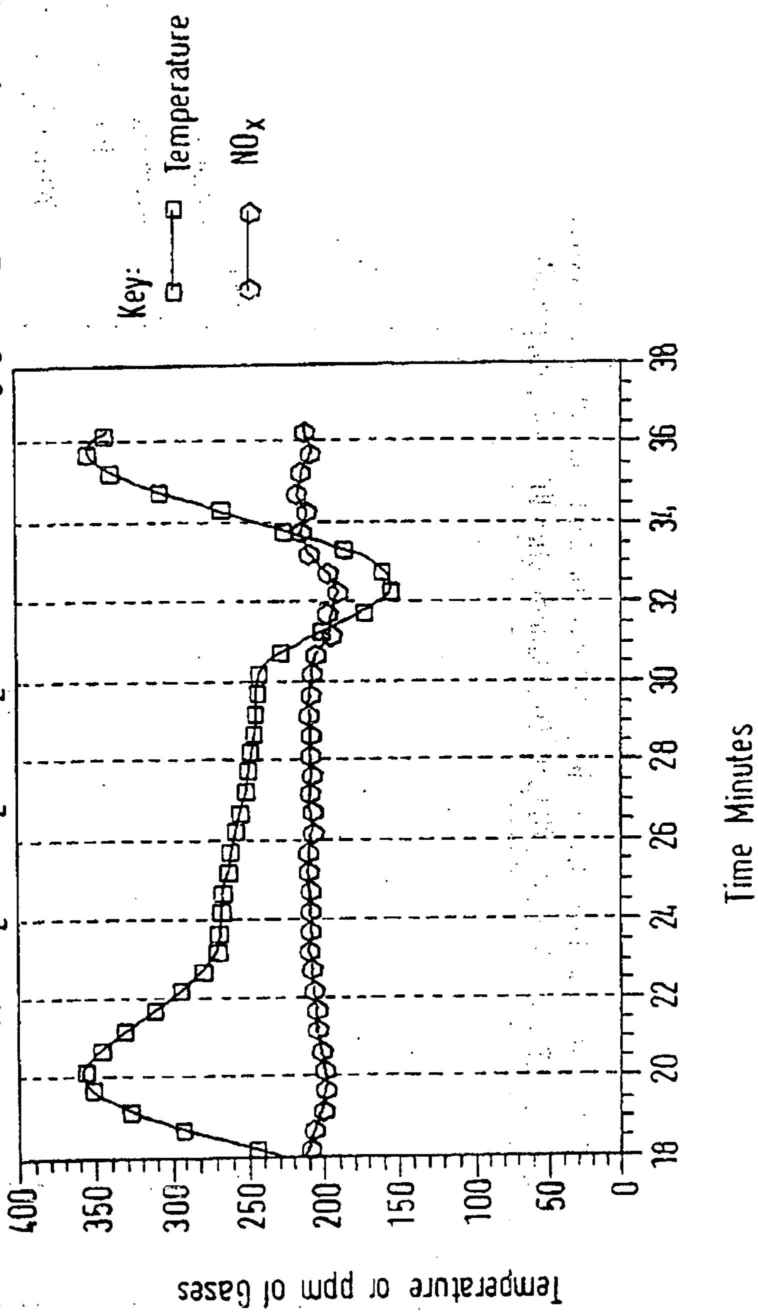


Fig.12. NO_x Activity of ZSM5 without NH_3 injection during cycle test
200ppm NO_2, 12% O_2, 14% CO_2, 200 ppm CO, 200ppm C_3H_6, 10% H_2O, 20ppm SO_2



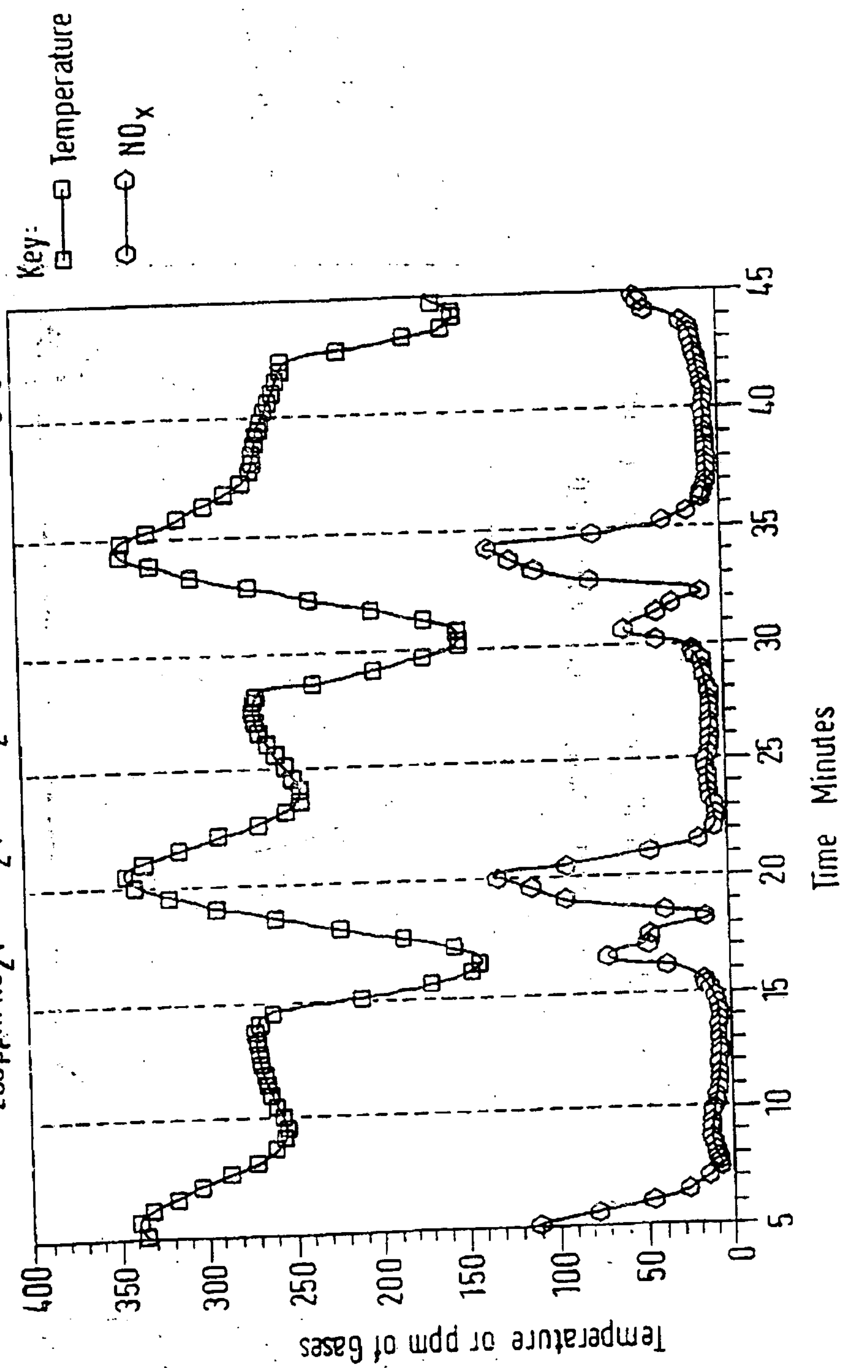


Fig. 13. Cycle NO_2 Activity of ZSM5 with NH_3 injection between 325°C to 250°C
200ppm NO_2, 12% O_2, 14% CO_2, 200ppm CO, 200ppm C_3H_6, 10% H_2O, 20ppm SO_2

Fig.14.

Effect of Adsorbed NH_3 on NO_x Activity of Cu/ZSM5

200 ppm NO, 12% O_2, 4% CO_2, 200 ppm CO

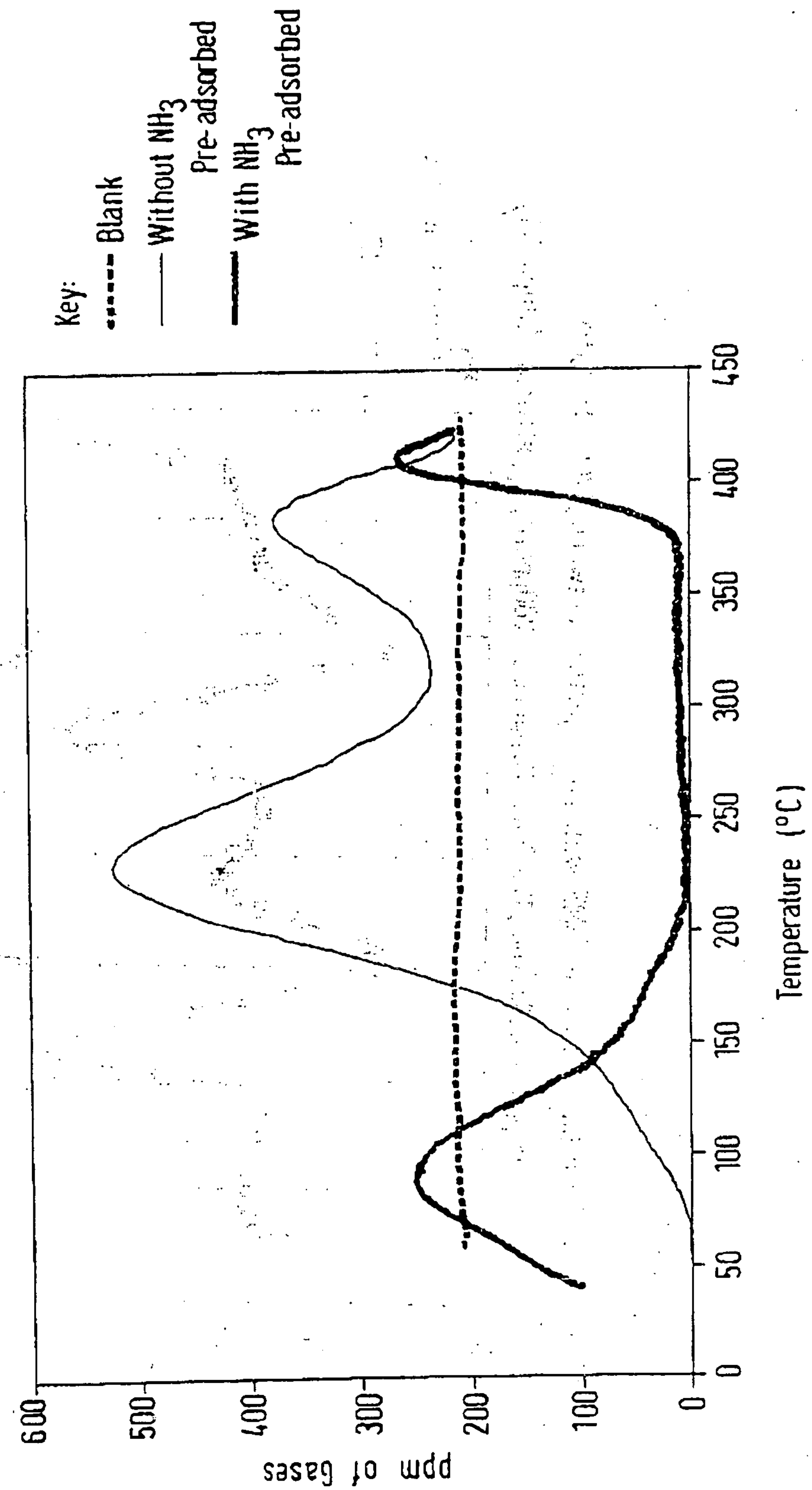
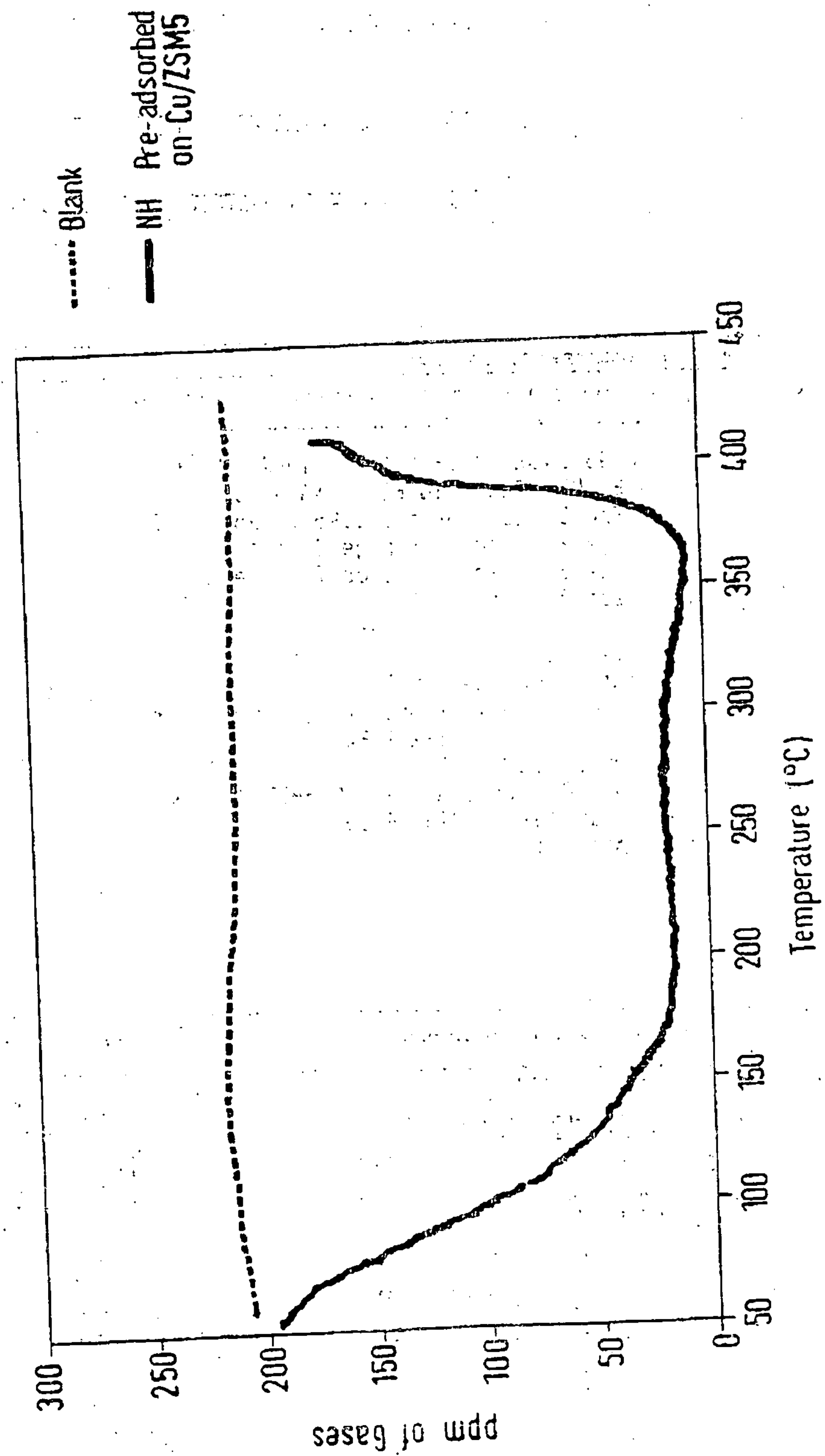


Fig.15. Effect of Adsorbed NH_3 on NO_x Activity of Cu/ZSM5 in Full gas mixture
200ppm NO, 12% O_2, 14% CO_2, 200ppm CO, 200ppm C_3H_6, 10% H_2O, 20ppm SO_2



INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01205

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94 B01D53/86 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 04980 A (HOFMANN LOTHAR ;MATHES WIELAND (DE); NEUFERT RONALD (DE); SIEMENS) 22 February 1996 (1996-02-22) page 2, line 18 - page 3, line 3 page 6, line 13 - page 7, line 2 page 8, line 16-26 ---	1-3,5,11
X	DATABASE WPI Section Ch, Week 9530 Derwent Publications Ltd., London, GB; Class E36, AN 95-227554 XP002111302 & JP 07 136465 A (BABCOCK-HITACHI KK), 30 May 1995 (1995-05-30) abstract ---	1-5,11

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 August 1999	23/08/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Polesak, H

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 99/01205

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 963 332 A (BRAND REINHOLD ET AL) 16 October 1990 (1990-10-16) column 2, line 11-17	1,4,11
X	EP 0 773 354 A (TOYOTA MOTOR CO LTD) 14 May 1997 (1997-05-14) page 21, line 25-29	1,6,9-11
A	US 5 369 956 A (MARQUARDT KLAUS-JUERGEN ET AL) 6 December 1994 (1994-12-06)	
A	US 5 628 186 A (SCHMELZ HELMUT) 13 May 1997 (1997-05-13)	

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01205

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 9604980	A	22-02-1996	AT	169841	T	15-09-1998
			CA	2197072	A	22-02-1996
			DE	59503286	D	24-09-1998
			EP	0775013	A	28-05-1997
			ES	2122602	T	16-12-1998
			JP	10501460	T	10-02-1998
			US	5785937	A	28-07-1998
JP 7136465	A	30-05-1995	NONE			
US 4963332	A	16-10-1990	DE	3825206	A	01-02-1990
			CN	1041288	A	18-04-1990
			EP	0362483	A	11-04-1990
			JP	2068119	A	07-03-1990
EP 0773354	A	14-05-1997	JP	9133032	A	20-05-1997
			US	5782087	A	21-07-1998
US 5369956	A	06-12-1994	DE	4217552	C	19-08-1993
			FR	2691645	A	03-12-1993
			GB	2267365	A,B	01-12-1993
			IT	1261461	B	23-05-1996
US 5628186	A	13-05-1997	DE	4315278	A	10-11-1994
			AT	143460	T	15-10-1996
			WO	9427035	A	24-11-1994
			DE	59400746	D	31-10-1996
			EP	0697062	A	21-02-1996
			ES	2091694	T	01-11-1996
			JP	8509795	T	15-10-1996

This Page Blank (uspto)